Fluctuation-dissipation theorem with applications in the electromagnetic field

Author: Joan Salas Llabrés.
*Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Catalunya, PPCC.**

Advisor: Agustí Pérez Madrid

Abstract: Not so far from equilibrium, a powerful relation exists between the dissipation of energy (or equivalently entropy production) of a given system out of equilibrium and its fluctuations. Moreover, dissipation is nothing but a measure of how intrinsic randomness and chaos affect the transport properties of a system out of equilibrium. This relation is manifested in the fluctuation-dissipation theorem (FDT), which is derived here, along with its quantum extension and an overview of the theory of linear response. The quantum version permits a way to understand its application to electromagnetic radiation (radiative heat transfer and an attractive force at the nanoscale), and will show how fluctuations of the electromagnetic field persist even at zero temperature.

I. INTRODUCTION

The fluctuation-dissipation theorem is ubiquitous in non-equilibrium statistical physics as well as the partition function is in equilibrium statistical thermodynamics. Roughly speaking, the FDT relates response functions of a thermodynamic system to its equilibrium properties. Hence, in the sense that it yields a relation between energy fluctuations and the heat capacity, one could say that Einstein's theory of fluctuations already offers us an earliest version of the FDT. After this, it followed Nyquist result relating voltage fluctuations and the resistance of a conductor [1]. Nyquist result was generalized by Callen and Welton [2] to establish the relation between instantaneous equilibrium fluctuations and the response to a driving force.

Fluctuations are caused by perturbations of the given equilibrium system, and they originate from internal and external constraints, like the presence of a heat bath, that thermally excites the constituents; or external random forces as random electromagnetic fields (a case we will deal with in the applications). We will show that the behaviour of these fluctuations can be modelled by random fields, and it is just the statistical correlation of this random field with itself at different times that constitute the FDT. Moreover, from the extension of the theorem to quantum mechanics, we will see how even in vacuum itself there are fluctuations, due to the existence of a zero-point energy which persists in the fundamental state, i.e. in zero temperature.

Historically, the natural framework of approach to this problem is Brownian motion, that is, the erratic motion of, for example, pollen grains in a liquid medium. Langevin was the first to relate macroscopic motion, with Newton's laws on one hand; and microscopic random forces, on the other, in a mesoscopic point of view that constituted the basis of the theory of stochastic processes. Then, the Brownian motion can be understood as the continuous relaxation of the velocity of the mesoscopic particle, which diffuses through the chaotic and incessant impacts with the other particles of the medium, being their random motion a consequence of the molecular chaos. The response function of the Brownian particle, the mobility, is computed with the aid of the FDT, leading to a Green-Kubo -like relation involving the velocity correlation function. Thus, a useful application of the FDT is that it allows one to compute and understand the transport coefficients of very different systems.

This article is structured as follows: in section II we will derive the FDT from the Generalized Langevin equation along with an overview of the theory of linear response. In section III we will deal with how to apply this results to electromagnetic radiation in a system of charges, deriving the quantum extension of the FDT. Finally in section IV we will provide the final remarks and conclusions about this fundamental problem in modern physics. An appendix is added with a description of the probability distribution of the Gaussian noise (which models the random field) in terms of functionals.

II. FLUCTUATION-DISSIPATION THEOREM

A. Classical derivation of the fluctuation-dissipation theorem through generalized Langevin equation (GLE)

Intuitively one could think of the motion of the Brownian particle as modelled by a Newtonian equation in which the erratic motion is caused by a random force field $F(t)$. In the majority of applications there is also an external deterministic field (gravity, in sedimentation of particles; or electromagnetic) that drives the motion of the particle and results in friction $-\gamma v(t)$, a resistive force which will turn out to be due to the multiple impacts with the surrounding particles.

Friction corresponds to the viscous drag $B = 1/\gamma$, the drift velocity acquired by the particle due to the unit external force. So, the response of the particle to the incessant collisions is reflected in a *systematic* part, the

*Electronic address: tfgac@ub.edu

friction force for the forced motion, as well as the *random* force that originates the stochastic trajectory, which of course averages to zero after long times in *statistical* thermal equilibrium [4]. Additionally in a first approximation, the nature of the random field is independent of the presence of the external field [4] (linear effect), but results in friction. Then the connection between the response of a given system to an external disturbance (like friction) and the internal fluctuation of the system in absence of the disturbance will be given by FDT [4].

Proceeding as in Ref. [5] and [6], it is clear that in Langevin's original approach, friction is modelled by the classical term $-\gamma v(t)$. This corresponds to an instantaneous response of the surrounding fluid to the changes in the coordinates of the mesoscopic particle. A more realistic description needs the friction to have some memory, as the fluid itself has a given inertia and depends on the motion of the particle in the past (from the time it was put in contact with the thermal bath) [5].

In general one can now consider a system which can be characterized by two coupled Brownian degrees of freedom $\alpha(t)$ and $\beta(t)$:

$$\frac{d\alpha}{dt} = \beta(t) \tag{1}$$

$$\frac{d\beta}{dt} = -\int_{-\infty}^{t} K(t-t')\beta(t')\,dt' + X(t) + F(t) \tag{2}$$

This last equation is the generalized or retarded Langevin equation (GLE), as it contains the retarded nature of the friction through the memory kernel $K(t)$; an external systematic force $X(t)$ is also considered. Taking into account the Central Limit theorem, the random force $F(t)$ corresponds to a stationary stochastic process with zero mean, a Gaussian and Markovian process. We assume as an hyphothesis:

$$\langle \beta(0)F(t)\rangle = 0 \tag{3}$$

The solution for the velocity can be obtained by using Laplace transforms:

$$\beta(t) = \beta(0)R(t) + \int_0^t R(t-t')[X(t') + F(t')]\,dt' \tag{4}$$

where we have introduced the memory function $R(t) = \mathcal{L}^{-1}\left[\frac{1}{s+\tilde{K}(s)}\right]$. Now the contribution of the external field can be embedded into the dynamical variable β redefining it as a purely diffusive process (without any external driving field):

$$\tilde{\beta}(t) = \beta(t) - \int_0^t R(t-t')X(t')\,dt' \tag{5}$$

which satisfies the equality:

$$\tilde{\beta}(t) = \tilde{\beta}(0)R(t) + \int_0^t R(t-t')F(t')\,dt' \tag{6}$$

For the FDT, we are trying to find a relationship between the autocorrelation function of the stochastic field $\langle F(t')F(t)\rangle \equiv C_F(t,t') = C_F(t-t')$ (assuming stationarity) and the memory kernel $K(t)$. Let us notice that:

$$\langle(\tilde{\beta}(t) - \tilde{\beta}(0)R(t))^2\rangle =$$

$$= \int_0^t d\tau \int_0^t d\tau' R(\tau)R(\tau')C_F(\tau'-\tau) \tag{7}$$

And also:

$$\langle(\tilde{\beta}(t) - \tilde{\beta}(0)R(t))^2\rangle =$$

$$= \langle\tilde{\beta}^2(t)\rangle + \langle\tilde{\beta}^2(0)\rangle R(t) - 2R(t)\langle\tilde{\beta}(0)\tilde{\beta}(t)\rangle \tag{8}$$

Both expressions are nothing but the variance of the random variable $\tilde{\beta}(t)$, i.e. its deviations from the averaged-equilibrium value, which considers the evolution only deterministic. Being the random process Gaussian and Markovian, we are only concerned with its second moment. If the system is in statistical thermal equilibrium, one can substitute the averages of the velocity $\tilde{\beta}(t)$ for the equipartition theorem value k_BT and make use of the result (8):

$$\langle(\tilde{\beta}(t) - \tilde{\beta}(0)R(t))^2\rangle = (1-R(t)^2)k_BT \tag{9}$$

To obtain this, the equality $\frac{\langle\tilde{\beta}(0)\tilde{\beta}(t)\rangle}{\langle\tilde{\beta}(0)^2\rangle} = R(t)$ has also been used, obtained from the generalized velocity equation (6). Using (7) we finally get:

$$k_BT(1-R(t)^2) = \int_0^t d\tau \int_0^t d\tau' R(\tau)R(\tau')C_F(\tau'-\tau) \tag{10}$$

Now we can derive with respect to t both sides of this last expression. On one hand we get for the left side:

$$\frac{d[k_BT(1-R(t)^2)]}{dt} = -2k_BTR(t)\frac{dR}{dt} =$$

$$= -2k_BT\frac{R(t)}{\langle\tilde{\beta}^2(0)\rangle}\left\langle \tilde{\beta}(0)\frac{d}{dt}\tilde{\beta}(t)\right\rangle \tag{11}$$

where the average is over the stationary noise, so the time derivative can be put into it. Now making use of the GLE to render the derivative of $\beta(t)$ we have:

$$\frac{d[k_B T(1-R(t)^2)]}{dt} = 2k_B T R(t)\int_0^t K(t-s)R(s)\,ds \tag{12}$$

On the other hand, the time derivative of the right side of (10) can be computed using the Leibniz's formula for differentiating integrals that depend on parameters, giving [3]:

$$\frac{d}{dt}\left[\int_0^t d\tau \int_0^t d\tau' R(\tau)R(\tau')C_F(\tau'-\tau)\right] =$$

$$= 2R(t)\int_0^t R(\tau)C_F(t-\tau)\,d\tau \tag{13}$$

Comparing (12) with (13) gives, for any value of the time integration variable:

$$k_B T K(t) = C_F(t) = \langle F(0)F(t)\rangle \tag{14}$$

which is known as the second fluctuation-dissipation theorem for the generalized Langevin equation. It relates the internal thermal fluctuations of an equilibrium quantity of the system, characterized by a correlation function, to the dissipative process connected to it, characterized by the response function $K(t)$ [3], [4], as we stated in the introduction. It is also remarkable that the GLE naturally deals with coloured noise [5], that is, the time dependence of the friction introduces an spectrum of frequencies to the autocorrelation function (somewhat form of the Wiener-Khintchine theorem [3]). Obviously, an instantaneous friction kernel $K(t) = \gamma\delta(t)$ recovers the more common form of the Langevin equation.

B. Linear response

In the first subsection the effect of the external field which drives the system from one equilibrium state to another was not fully taken into account but absorbed into $\tilde{\beta}(t)$. Now one can deal with its effects in some dynamical variable $x_j(t)$ of the system (analogous to $\alpha(t)$), which will accordingly fluctuate from the equilibrium value due to the application of a generalized field $X_j(t)$ as $\delta x_j(t) = x_j(t) - \langle x_j\rangle$. In this way we can write the interaction Hamiltonian for a small perturbation [8]:

$$\delta H(t) = -c_j x_j X_j(t) \tag{15}$$

which expresses the coupling between the perturbation and the significant fluctuating quantity (generalized displacement) x_j, proper to systems not far from equilibrium. Later on (15) will be taken into account when dealing with the electromagnetic field.

Proceeding as in Ref. [9], in statistical mechanics we can deal with the evolution of the quantities describing an ensemble of systems by means of the known distribution ρ at $t = 0$. Then the expectation value of the dynamical variable $x_j(t)$, which is determined by the phase space coordinates denoted $[\boldsymbol{r}^N(t); \boldsymbol{p}^N(t)] \equiv s$, will be given at later time by:

$$\overline{x_j(s,t)} = \frac{\int \rho(s)x_j(s,t)\,ds}{\int \rho(s)ds} \tag{16}$$

In view of the applications, one shall consider now the special case of a field $F(t)$ switched off at $t = 0$ from a constant value in the past. It is remarkable to notice that the system is in equilibrium with the applied perturbation, so one can deal here with the relaxation of the system from one equilibrium state to the other, experiencing a change of *inertia*. Considering the canonical equilibrium distribution for the particles prior to the relaxation, with $H(t) = H_0 + \delta H(t)$ the total Hamiltonian, and being the perturbation small, one has:

$$\rho(t) \propto e^{-[H_0+\delta H]/k_B T} = \rho_0 e^{-\delta H/k_B T} =$$

$$= \rho_0\left[1 - \frac{1}{k_B T}\delta H + O(\delta H)^2\right] \tag{17}$$

where ρ_0 is the distribution function of the "equilibrium" state, i.e. the unperturbed one. With this equation in mind, the expectation value of the dynamical variable (16) reads:

$$\overline{x_j(t)} = \langle x_j\rangle - \beta[\langle \delta H x_j(t)\rangle - \langle x_j(t)\rangle\langle \delta H\rangle] + O(\delta H)^2 \tag{18}$$

where $\langle\rangle$ denotes the average for the unperturbed state. After rearranging, we can take into account $\delta\overline{x_j(t)} = \overline{x_j(t)} - \langle x_j\rangle$ and due to the time-translational invariance of the Hamiltonian, we can take $t = 0$, when the perturbation stops. And thus, we obtain:

$$\delta\overline{x_j(t)} = \beta c_j X_j[\langle x_j(0)x_j(t)\rangle - \langle x_j(0)\rangle\langle x_j(t)\rangle] \tag{19}$$

The term in brackets is nothing but the component $(0,t)$ of the covariance tensor for the generalized displacement, that can be written as:

$$\delta\overline{x_j(t)} = \beta c_j X_j \langle \delta x_j(0)\delta x_j(t)\rangle \tag{20}$$

This result equates the time dependence of the decay of a prepared perturbation to the time dependence of the autocorrelation function in the unperturbed system, which can be interpreted as a response function. Now, for a general $F(t)$, an according relationship shall be expected between the response or susceptibility function and the deviations due to the external field. The linear response now states:

$$\delta\overline{x_j(t)} = \int_{-\infty}^{\infty} \chi_{jk}(t,t')X_k(t')\,dt' \tag{21}$$

as in [9] and [10]. $\chi_{jk}(t,t')$ has the important property of stationariety. Combining this with the expression for the step function field turned off at $t' = 0$ we arrive at the classical Kubo expression [9]:

$$\chi_{jk}(t) = -\frac{1}{k_B T}\Theta(t)\frac{d}{dt}\langle \delta x_k(0)\delta x_j(t)\rangle \tag{22}$$

where the Heaviside step function $\Theta(t)$ is introduced to ensure causality ($\chi_{jk}(t) = 0$ for $t < 0$) [10].

III. APPLICATIONS. ELECTROMAGNETIC RADIATION

A. Quantum extension

In view of an interesting and practical application of FDT we will consider next, we shall give its quantum extension, as to apply it to a collection of charged particles in equilibrium with a thermal bath where the action of an electromagnetic field is considered. This perturbation drives the charges locally out of equilibrium, provoking both charge and current fluctuations, exciting fluctuating multipoles. Note that the relaxation due to the external driving field adds an extra source of fluctuations to the system, besides the thermal origin.

These fluctuations in turn induce a stochastic electric field which interacts with the multipoles and closes the circle. In first approximation we will consider only dipoles, being the interaction Hamiltonian $\delta H = -\boldsymbol{\mu}(s,t)\boldsymbol{E}(t)$, as in (15). So, in computing the contribution to the force acting on a polarizable particle, as Novotny presents, it should be considered that both field and dipole moment have fluctuating and induced parts [10].

$$\langle \boldsymbol{F}(\boldsymbol{r}_0)\rangle = \langle \mu_i^{(\mathrm{in})}(t)\nabla E_i^{(\mathrm{fl})}(\boldsymbol{r}_0,t)\rangle + \langle \mu_i^{(\mathrm{fl})}(t)\nabla E_i^{(\mathrm{in})}(\boldsymbol{r}_0,t)\rangle \tag{23}$$

As it is clear from equilibrium statistical mechanics, due to the external perturbation $\boldsymbol{E}(\boldsymbol{r},t)$ the instantaneous expectation value of the dipole moment will deviate from its equilibrium average $\delta\overline{\boldsymbol{\mu}} = \overline{\boldsymbol{\mu}} - \langle\boldsymbol{\mu}\rangle$, as in last section. So it plays the role of the random field in our framework (or better said, it is a stochastic process caused by the random force exerted on the system) and we could expect that its correlation will be related to some dissipative property. According to the linear response theory we just developed, i.e. assuming a small deviation that depends linearly on the external perturbation, (21) adopts the form [10]:

$$\delta\overline{\mu_j(t)} = \frac{1}{2\pi}\int_{-\infty}^{t} \tilde{\alpha}_{jk}(t-t')E_k(t')\,dt' \tag{24}$$

With $\tilde{\alpha}_{jk}(t-t')$ the polarizability that expresses, like in the GLE framework, that the system does not respond instantaneously to the perturbation. From here, following previous procedures we can arrive at an equivalent Kubo expression (22) [10]:

$$\tilde{\alpha}_{jk}(t) = -\frac{2\pi}{k_B T}\Theta(t)\frac{d}{dt}\langle \delta\mu_k(0)\delta\mu_j(t)\rangle \tag{25}$$

This is often referred as the time-domain FDT, and it states that the system's response to a weak external field can be expressed in terms of the system's fluctuation of the equilibrium state, i.e. in absence of the external field [10] (recall that the average is computed using the equilibrium distribution). Furthermore, it is more practical to express the theorem in the frequency domain, for it we can use the Fourier transform of the above quantities and the Wiener-Khintchine theorem, which connects the time autocorrelation function to its power spectrum for a random process (see [3] for more detail and discussion on the theorem). We obtain [10]:

$$[\alpha_{jk}(\omega) - \alpha_{jk}^*(\omega)]\delta(\omega-\omega') = \frac{2\pi i\omega}{k_B T}\langle \delta\hat{\mu}_j(\omega)\delta\hat{\mu}_k(\omega')\rangle \tag{26}$$

The spectral representation of the FDT, valid in classical mechanics. Now we should take into account the fact that, according to quantum mechanics, the modes of oscillation can only assume discrete energy values; so the continuous average energy per degree of freedom $k_B T$ (as expressed by the equipartition theorem) should be replaced by $\frac{\hbar\omega}{\exp(\hbar\omega/k_B T)-1} + \hbar\omega$, which corresponds to the mean energy of the quantum oscillator plus the zero-point energy, respectively [10]. Substituting into (26) renders:

$$\langle \delta\hat{\mu}_j(\omega)\delta\hat{\mu}_k(\omega')\rangle =$$

$$= \frac{1}{2\pi i\omega}\left[\frac{\hbar\omega}{1-e^{-\hbar\omega/k_B T}}[\alpha_{jk}(\omega)-\alpha_{jk}^*(\omega)]\right]\delta(\omega-\omega') \tag{27}$$

the quantum version of the FDT. Notice that purely quantum fluctuations of the electromagnetic field are allowed at zero temperature.

Furthermore, (27) can be generalized for a fluctuating current density in an isotropic and homogeneous medium with dielectric complex constant $\epsilon(\omega) = \epsilon' + i\epsilon''$ [10]:

$$\langle \delta\hat{j}_j(\boldsymbol{r},\omega)\delta\hat{j}_k(\boldsymbol{r}'\omega')\rangle =$$

$$= \frac{\omega\epsilon_0}{\pi}\epsilon''(\omega)\left[\frac{\hbar\omega}{1-e^{-\hbar\omega/k_B T}}\right]\delta(\omega-\omega')\delta(\boldsymbol{r}-\boldsymbol{r}')\delta_{jk}. \tag{28}$$

B. Molecular attractive forces and radiative heat transfer

The result of charge and current correlations create a fluctuating electromagnetic field that mediate in between neutral bodies in the nanoscale, giving rise to dispersion forces and radiative heat transfer between them when the spacing is comparable to the wavelength of the dominant vacuum fields involved. Novotny and Hecht provide an overview of this effects in the case of the force between two little polarizable particles (the Van der Waals and Casimir forces) and the dissipation of energy by a body made up of these fluctuating point sources, and reaches the Planck blackbody formula [10].

Lifshitz, along with Polder and Van Hove, respectively in [11] and [12] derived the expressions for the general case of two different *bulk* materials at an arbitrary temperature (the same for both bodies in the first) with the aid of the FDT. In both ideal scenarios thermal equilibrium of the sources of the individual bodies (charges) with the electromagnetic radiation field is required, as it is the case for closed systems.

On account of this, the authors proceed in a *purely macroscopic fashion* [11], adding to Maxwell's equations an inhomogeneous extra term for the thermally fluctuating currents. This gives rise to a local stochastic electric field [10], analogous to the random field in the GLE framework. The microcurrents in the substance constitute the noise sources of the force and thermal radiation, in the form of evanescent propagating waves which interact with each other in vacuum. This explains the strong dependence on the separation of the two bodies, that is, the interaction phenomena are enhanced if the gap distance is sufficiently small [12]. Also, it is important to notice the dependence on the specific dielectric properties of the materials encapsulated in the complex $\epsilon(\omega)$.

The random source corresponds to a Gaussian variable, so a FDT is expected for the random fields in order to compute the statistical averages leading to the expressions of the force and heat transfer. This is done in the form of equation (28) for the current density $\boldsymbol{j}(\boldsymbol{r}, t)$ derived in the last subsection. In the first case it is applied to the Maxwell stress tensor [11] and in the second, to the averaged Poynting vector. The latter is not zero in each body, permitting transport between them to reach and maintain thermal equilibrium [12].

Clearly, this results match the limiting case discussed by Novotny for sufficiently rarified bodies (like gases), in which the individual interactions between atoms can be taken into account.

IV. CONCLUSIONS

To conclude, it should be emphasized how the FDT gives a deep understanding on why there exist friction, electric resistance or even forces acting on the nanoscale, and are nothing but the response of a system to the dissipative processes operating when it is not far from equilibrium. This has been explicitly seen on the basis of linear response theory, in the way as we have only dealt with *perturbations* up to linear order in the significant variable. The source of fluctuations has also been discussed, and when extending the theorem to quantum mechanics it has revealed how not all of them are of thermal origin.

Furthermore, it is remarkable to mention that efforts are made to generalize it to systems far away from equilibrium. That can be done introducing properly the concept of effective temperature [6].

Acknowledgments

I would like to thank my advisor, Dr. Agustí Pérez, for the patience and knowledge on how a physicist works; also to Dr. Ivan Latella for fruitful discussions. I would like to express my gratitude to my family for the unconditional and practical support, to my mother for the grammar revision, to all my friends and last but not least, to Neus Alert for never stopping believing in me.

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Appendix

A. Description in terms of functionals. Gaussian noise distribution functional

In this article we have dealt with a random force $F(t)$, the correlation at different times of which was expressed by the second FDT (14). From here, considering it as a Gaussian noise distribution, our goal is to express its distribution functional in Dirac notation (bras and kets).

The random force takes values in time from 0 to infinity, so technically it pertains to a space of functions defined in the interval $0 \leq t < \infty$ and can symbolically be represented by a ket $|F\rangle$. In this form, it is easier to deal it with Dirac notation, which naturally provides a way to generalize a vector in conventional 3-dimensional space to any dimension vector space as a function space.

Every value the random force takes can be thought of a random variable, each component of a infinite length element $|F\rangle$ pertaining to the function space (which is no more than a vector space of infinite dimension), corresponding to the projection of the element on the canonical base. This is easily identified with every value of the time parameter, $F(t) = \langle t|F\rangle$, which is continuous.

The FDT we derived says:

$$\overline{F(t')F(t)} = k_B T K(t-t') \equiv H(t,t') \tag{29}$$

from we can identify $H(t,t')$ as the (t,t') component of the covariance tensor $\boldsymbol{H}$, $\langle t|\boldsymbol{H}|t'\rangle$ (notice the change of notation for the equilibrium average). Using the expression for the components of the force we can write:

$$\overline{|F\rangle\langle F|} = \boldsymbol{H} \tag{30}$$

The Gaussian distribution of a single random variable x with zero average is as follows:

$$f(x) = N^{-1} \exp\left\{-\frac{1}{2}\frac{x^2}{\sigma^2}\right\} \tag{31}$$

being N the normalization constant. We know that for a single variable, $\mathrm{Cov}(x,x) = \sigma^2 \equiv H$, i.e. the covariance equals the variance. Here we can identify $\frac{x^2}{\sigma^2} = x \cdot \frac{1}{\sigma^2} \cdot x = x \cdot H^{-1} \cdot x$ and thus, analogously $\langle x|\boldsymbol{H}^{-1}|x\rangle = x_i(\boldsymbol{H}^{-1})_{ij}x_j$. Then the functional generalization can be done by replacing the single random variable x with the random function F:

$$f(|F\rangle) = N^{-1} \exp\left\{-\frac{1}{2}\langle F|\boldsymbol{H}^{-1}|F\rangle\right\} \tag{32}$$

With the term into brakets given by:

$$\langle F|\boldsymbol{H}^{-1}|F\rangle = \int_0^\infty dt \int_0^\infty dt' \langle F|t\rangle\langle t|\boldsymbol{H}^{-1}|t'\rangle\langle t'|F\rangle =$$

$$= \int_0^\infty dt \int_0^\infty dt' F(t) H^{-1}(t,t') F(t) =$$

$$= \int_0^\infty dt \int_0^\infty dt' F(t) \frac{K(t,t')^{-1}}{k_B T} F(t) \tag{33}$$

where we have used the FDT, the identity completeness relation and the fact that due to the function space is real we can write $\langle F|t\rangle = \langle t|F\rangle^* = \langle t|F\rangle$.

Rendering this into (32) gives the common representation of the functional, here the Gaussian noise distribution, and we will refer to it as $f\{F(t)\}$. The normalization constant can be computed with aid of the path integral [5]:

$$N = \int f\{F(t)\}\, \mathcal{D}F(t) \tag{34}$$

where the integral is performed over all (infinite) values of the function $F(t)$, with the differential given by:

$$\mathcal{D}F(t) = \lim_{n\to\infty} dF_1 dF_2 \ldots dF_{n-1}. \tag{35}$$

B. Mobility of the Brownian particle

The second FDT offers an easy way to compute the mobility of the Brownian particle. From (14) we know:

$$K(t-t') = \frac{1}{k_B T}\langle F(t')F(t)\rangle \tag{36}$$

Integrating both sides:

$$\int_{-\infty}^{\infty} K(t-t')\, dt' = \frac{1}{k_B T}\int_{-\infty}^{\infty} \langle F(t')F(t)\rangle\, dt' \tag{37}$$

we can identify, with the aid of (2) and analogous to the original Langevin equation, the left side of (37) as the inverse of the mobility B:

$$\frac{1}{B} = \frac{1}{k_B T}\int_{-\infty}^{\infty} \langle F(t')F(t)\rangle\, dt' \tag{38}$$

And now, from [3] we know the useful relation:

$$\int_{-\infty}^{\infty} \langle v(t')v(t)\rangle\, dt' \int_{-\infty}^{\infty} \langle F(t')F(t)\rangle\, dt' = (k_B T)^2 \tag{39}$$

that substituted into (38) yields the relation:

$$B = \frac{1}{k_B T}\int_{-\infty}^{\infty} \langle v(t')v(t)\rangle\, dt' \tag{40}$$

the Green-Kubo relation for the mobility B.